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(54) Title: FLAME RETARDANT POLYMER COMPOSITES AND METHOD OF FABRICATION

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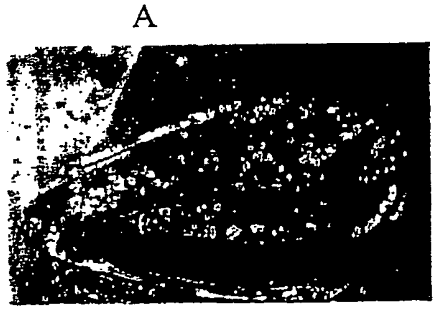

B

(57) Abstract: FLAME RETARDANT POLYMER COMPOSITES AND METHOD OF FABRICATION A flame retardant composite and a method for its fabrication are disclosed. The flame retardant composite shows both improved mechanical properties and flame retardancy. The composite comprises a matrix material and carbon nanotubes, such as single walled nanotubes, multi-walled nanotubes or fishbone-like graphitic cylinders, exhibiting a hollow core. For example, the outer diameters of the carbon nanofibers may be in the range from 1.2 to 500 nm. For example, a carbon nanotube may be incorporated as a layer in or on the surface of the composite. The method of fabrication of the composite may include a step of de-agglomeration.

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FLAME RETARDANT POLYMER COMPOSITES AND METHOD OF FABRICATION

RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application No. 60/359,276, filed February 20, 2002.

FIELD OF THE INVENTION

[0002] The present invention relates to a flame retardant polymer composite and a method for its fabrication. One embodiment is a flame retardant polymer composite reinforced by embedded carbon nanotubes that impart flame retardancy and improved mechanical properties. Flame retardant polymer composites made according to the method of fabrication have a higher impact strength and stiffness than other flame retardant polymer composites.

BACKGROUND OF THE INVENTION

[0003] It is known that the addition of fibers to a matrix material can substantially improve the mechanical properties of a part or structure compared to the mechanical properties of the matrix material without the addition of fibers. For example, fibers of straw were used in mud bricks for residential construction from the time that civilized people first began constructing villages. Also, fiberglass, a composite of a polymer with glass fibers, is used ubiquitously in residential and commercial construction and in the transportation sector, providing light weight, high strength and low cost. Composites comprising a polymer matrix and carbon fiber reinforcement are also known in the art.

[0004] Many polymers are inflammable (i.e. subject to combustion and burning if exposed to high temperatures or flames). Textiles, materials used in transportation, and materials for construction, remodeling or repair of residential or commercial real estate must meet certain minimum safety

standards, including increasingly stringent fire safety codes. Polymeric materials and composites based on polymers or epoxy resins offer light weight, durability, and low cost of a large number of applications in textiles, and in construction, including but not limited to waste pipes, furniture, clothing, insulation, wall coverings, and load bearing members. Polymers that are inflammable at temperatures that can be expected to be encountered in the service life of a product, part or structure either by accident or design are undesirable. Furthermore, some polymers emit noxious or toxic fumes when burning, which can substantially increase the number of injuries and deaths, as a result of an accidental combustion of the polymeric material. Furthermore, materials based on polymers or epoxy resins require flame retardancy in transportation, e.g. aircraft parts and automobile parts, and in construction of residential and commercial buildings, must be designed to. In addition, polymeric textiles require flame retardancy for clothing, including protective helmets, flame retardant clothing, flame retardant and durable upholstery, and flame retardant and ballistic-impact-resistant structures, vests and shelters.

[0005] The typical solution to the problem of inflammability of epoxy resins and polymeric materials used in these applications and others is to combined flame retardant additives with the epoxy resin, curing agent or polymer matrix of the material or composite. The term flame retardant is being used herein to mean the ability to retard the spread of an existing flame, to deter the ignition of a polymer-based material exposed to a flame, and to resist degradation of a polymeric-based materials mechanical properties for a period after exposure to heat and flame in a fire. Generally, one or more specific additives are selected for particular polymeric materials and can reduce inflammability, prevent combustion, reduce toxic emissions, cause the material to self-extinguish and/or reduce the subsequent rapid spread of fire once combustion occurs. For example, flame retardants include halogen-containing or phosphorous-containing organic compounds. Once exposed to high temperatures the polymer composites with additives can be a source of non-inflammable gases, phosphoric acid or some

other blowing agent. A typical method of protection involves the rapid production of a multicellular foam at the surface of the polymer composite material at an elevated temperature, which acts as a non-inflammable barrier between the source of heat or flame and the polymer composite material.

[0006] More specifically, fire retardant grades of polymeric materials and composites based on polymer or epoxy resin matrices may be obtained by the incorporation of conventional additives which are generally either inorganic, for example magnesium hydroxide, or halogenated organic materials for example tris(β-chloroethyl) phosphate with antimony oxide as synergist. The inorganic flame retarding additives, if used in sufficiently large quantities, can adversely affect the physical and mechanical properties of the material or composite. The halogenated, organic additives resist ignition and retard combustion, but if exposed to an external flame, these additives can cause emission of toxic and extremely corrosive gases, which can result in serious injuries and severe degradation of aluminum and steel structures.

[0007] For example, U.S. Pat. No. 4,014,829, Baird et al., issued on Mar. 29, 1977, and British Pat. Specification No. 1,438,067, published on June 3, 1976, disclose flame retardant textile fibers which are obtained by impregnating poly(m-phenylene isophthalamide) fibers with tetrakis hydroxymethyl phosphonium compound and a resin containing active hydrogen (e.g., melamine-formaldehyde resin), and heating the impregnated fibers to form a cross-linked reaction product of the tetrakis hydroxymethyl phosphonium compound and the resin in the fibers. Poor fiber qualities and insufficient resistance to heat shrinkage are disadvantages of this method.

[0008] U.S. Pat. No. 4,008,345, Imanaka et al, issued on Feb. 15, 1977, discloses a process for fire-proofing treatment of shaped articles of aromatic polyamide which comprises contacting a shaped article of an aromatic polyamide with an aqueous solution of a halogen- and sulfur-free, phosphorus-containing inorganic acid, drying at a temperature ranging from about 150.degree C., and then post-treating at a temperature ranging from about 300.degree. C. to

about 450.degree. C. This method reduces the quality of fibers and provides inadequate protection against heat shrinkage and inflammability.

[0009] An improved non-inflammable epoxy resin was obtained by incorporating polyvalent alcohol, as a source of carbon, in epoxy resin in combination with a source of phosphorous and a source of non-inflammable gases. *See* U.S. Pat. No. 3,981,832. Upon heating, the polyvalent alcohol, as a source of carbon atoms, entered into an esterifying reaction with the phosphoric acid, which was produced by heating the phosphorous containing compounds. Immediately, the heat caused the ester to decompose, producing water, carbon dioxide, and other non-inflammable gases as bi-products of the reaction, which in combination with the other source of non-inflammable gases produces a foaming, wet barrier to the source of heat or flames. In addition, the phosphoric acid is recovered during the decomposition of the ester, and it continued to react, so long as the polyvalent alcohol was available to continue to esterifying reaction and the temperature remained sufficiently high to decompose the complex ester created. The chemical reactions at high temperature rendered the epoxy resins non-inflammable in a higher degree than known before, but the reaction was limited to articles made from epoxy resins and still required additives for the source of phosphoric acid and non-inflammable gases. The disclosed composition rendered molded articles non-inflammable without increasing the melting temperature of the disclosed epoxy resins or curing against above room temperature, reducing processing costs; however, glass fibers, not the hydrocarbon used as the source of carbon, were used to reinforce the epoxy resin.

[0010] Another solution to make a thermosetting polymer material flame retardant was to incorporate a low-melting-temperature glass powder and a blowing agent in the polymer matrix, which caused a layer of the glass to form at the surface of the polymer, reducing the amount of smoke produced compared to the use of halogen-producing additives. *See* U.S. Patent No. 3,933,689. Again, the low-melting-temperature glass powder was not used to improve the mechanical properties of the polymer.

[0011] One problem not generally addressed is the deleterious effect of each of the foregoing additives on the notched impact strength, toughness, strength and stiffness of the polymer composite. Another problem of adding halogen-containing or phosphorous-containing compounds is that these organic compounds often diffuse away over time, reducing the effectiveness of the flame retardancy over time. Yet another problem results from fixing halogen atoms into the epoxy resin or curing agent, which can cause an increase in the melting point of the epoxy resin or the curing agent. This can require the use of solvents to be able to mix the epoxy resin and curing agent at room temperature or the use of elevated temperatures for mixing, which add substantial costs to the production of parts or structures. Also, some of these additives reduce the combustibility, but nevertheless the polymer or polymer composite produces smoke, noxious fumes or toxic fumes at elevated temperatures.

[0012] An additional problem results from the addition of fibrous reinforcements, which act as a wick in polymer matrix materials. *See* U.S. Pat. No. 6,196,832. Glass fibers, ceramic fiber and carbon fiber can serve as heat-resistive wicks. Carbon fibers are particularly suited, because they are often both porous and heat-resistive, drawing up the liquified inflammable polymer, which vaporizes from the surface and ignites on contact with a flame. This wicking effect increases the difficulty in extinguishing combustion of a polymer matrix composite material. Also, it can reduce the effectiveness of additives for flame retardancy by wicking inflammable vapors through a flame retardant surface layer.

[0013] Fiber-reinforced polymer composite materials are being used to an increasing extent as replacements for steel and other structural materials, because fiber-reinforced polymer composites offer the advantages of lighter weight, improved corrosion resistance, and reduced maintenance requirements. Matrix resins used in such composites include, but are not limited to, polyesters, epoxy resins, phenolic resins, bismaleimides, and polyphenylene sulfides. Reinforcing materials include glass fiber, carbon fiber, Kevlar® fiber (a

registered trademark of E.I. du Pont Nemours and Company), and Spectra® fiber (a registered trademark of AlliedSignal, Inc.). *See* U.S. Pat. No. 5,236, 773, which discloses fire-resistant barrier materials include ceramic fabrics, ceramic coatings, and intumescent (swelling or foaming) coatings, and combinations of ceramic coatings with intumescent coatings to protect carbon-fiber reinforced polymer composites (including graphitic carbon-fibers). Also, U.S. Pat. No. 5,236,773 shows that graphitic carbon-fiber reinforcement provides little, if any, increased flame retardancy (e.g. graphite fiber reinforced epoxy resin composite and graphite fiber reinforced vinyl ester resin composite) compared with glass fiber reinforced polymer composites. Residual flexural strength is particularly poor for graphite fiber reinforced epoxy resins. The ceramic coatings with intumescent coatings add significant costs and parasitic weight to the structures. Also, ceramic coatings are brittle and can be undermined by the impact of a foreign object with the coated structure (e.g. an aircraft) and as a result of earthquakes.

[0014] Flame retardancy is experimentally determined by a series of standard test procedures, some such tests include Smoke Generation and Combustion Gas Products, ASTM E-662; and Residual Flexural Strength, ASTM D-790; which are incorporated herein by reference in their entirety. Also, additional inflammability tests are disclosed by Carlos J. Hilado in *Inflammability Handbook for Plastics*, 4th Ed., Technomic Publishing Co., Lancaster, Pennsylvania (1990), hereinafter referred to as "Hilado", including tests for smolder susceptibility of home furnishings, ignitability (e.g. ASTM D 1929), flash-fire propensity (e.g. Douglas flash-fire test), flame spread (e.g. ASTM E 84 and ASTM E 162), heat release (e.g. ASTM E 906 and ASTM E 5), fire endurance (e.g. ASTM E 119), ease of extinguishment (e.g. ASTM D 2863), smoke evolution (ASTM E 662 and ASTM D 2843), toxic gas evolution (German DIN 53436), and corrosive gas evolution (French CNET test). On page 108 of Hilado a chart of the characteristics of certain sources of ignition are shown, and this is incorporated herein by reference.

SUMMARY OF THE INVENTION

[0015] The present invention is directed to an improved flame retardant polymer composite and a method for its fabrication, which not only inhibits combustion, rendering the polymer composite non-inflammable or substantially reducing composite inflammability, but also improves the mechanical properties of the polymer composite. Preferably, a flame retardant polymer composite reinforced by carbon nanotubes retains some of its strength, stiffness, and toughness for a significant duration during exposure to high temperatures. Furthermore, the flame retardant properties of the carbon nanotubes eliminates the problem of wicking. The inventor's use of the terms flame retardant, flame retardance, and flame retardancy should be understood to include flame resistance and fire resistance, as these terms are commonly used in the art.

[0016] In one preferred embodiment of the invention a polymer composite comprises a polymer and a plurality of carbon nanotubes as reinforcements within the polymer composite. In this particular embodiment, a process mixes the plurality of carbon nanotubes into the polymeric matrix material, reinforcing the polymer matrix and rendering the composite flame retardant and antistatic. This embodiment of the invention may comprise additional additives, such as stabilizers, mold releasing agents, lubricants, antistatic agents, pigments, ultraviolet absorbers, organic halogen flame retardants, and inorganic flame retardants. The resulting composition may be further processed including, but not limited to, extruding, molding stamping, expanding, foaming and trimming. Following any subsequent processing, the resulting article or structure retains at least some of the improved mechanical properties and flame retardancy contributed by the addition of the carbon nanotubes.

[0017] In an alternative embodiment, the carbon nanotubes are incorporated within a polymer as reinforcing fibers at a concentration sufficient

to provide a level of fire retardancy desired for a particular application. The level of fire retardancy required is set by statute, building codes, federal or state guidelines or corporate policy. The level of fire retardancy obtained for a specific polymer matric with a specific volume or weight percent of carbon nanotubes that are incorporated by a specific process is easily determined using the tests that have been incorporated herein by reference that are found in the background section. In a typical embodiment, the polymer is melted in a compound engine and mixed therein with the carbon nanotubes. Preferably, water and other gases are removed or degassed to prevent the formation of voids in finished products, which can reduce fatigue life and strength. In one embodiment, the mixture is fed to an extruder and extruded into filaments or sheets. In an alternative embodiment, the carbon nanotubes are mixed directly in an extruder together with a polymeric material. In either embodiment, carbon nanotubes will typically be added to the polymer in a concentration in a range between about 10% and 60% by volume. Typically, 25% by volume of nanotubes in the surface layer of polymer resin matrix is sufficient to impart excellent flame retardancy. However, some beneficial fire retardancy is obtained with as little as 1% by volume of carbon nanotubes.

[0018] In an alternative embodiment, the carbon nanotubes are preferentially distributed with a higher density near the surface of a composite structure. In yet another embodiment the carbon nanotubes reinforce polymer filaments, which are used to produce textiles. In this embodiment the longitudinal axis of the carbon nanotubes are oriented preferentially along the longitudinal axis of the polymer filaments. These composite filaments are both non-inflammable and have excellent mechanical properties.

[0019] One object of the invention is to reduce the inflammability of the polymer composite. Another object of the invention is to improve mechanical properties of the composite including, but not limited to, the strength, toughness, impact resistance, and stiffness. Yet another object of the invention is to retain some residual tensile strength during a fire.

[0020] In another preferred embodiment of the invention, the carbon nanotubes are not incorporated within the matrix of a polymer, but the carbon nanotubes are incorporated within a textile including both polymeric filaments and filaments of the carbon nanotubes. In one particular embodiment, the filaments of carbon nanotubes are coated with a thin coating of polymeric material, which can be the same polymeric material comprising the unreinforced polymeric filaments or a different polymeric material than the unreinforced polymeric filaments. In one specific example, an aramid filament is reinforced with carbon nanotubes that are coated with an aramid material to produce a protective vest that is both highly resistant to inflammability and resists ballistic impacts. For example, a "bulletproof vest" provides protection from the ballistic impact of bullets and shrapnel, including both flame retardancy and protection from a ballistic projectile. Alternative embodiments include, but are not limited to, protective helmets, flame retardant clothing, flame retardant and durable upholstery, and flame retardant and ballistic-impact-resistant structures and shelters.

[0021] In yet another embodiment of the invention, the carbon nanotubes are impregnated within and around a cotton textile. In an alternative embodiment, the carbon nanotubes are impregnated within and around a polymeric textile. In a specific embodiment, the impregnated textile can be subsequently incorporated as a layer within a composite structure. For example, the impregnated textile can be incorporated as a layer in a multilayer panel with an epoxy resin matrix. In one specific embodiment, the multilayer panel is prepared by hand lay-up, is enclosed in a vacuum bag, and is cured in an autoclave to yield a high-quality composite panel that has good tensile strength, flame retardancy, and antistatic properties.

BRIEF DESCRIPTION OF THE FIGURES

[0022] For the purpose of illustrating the invention, representative embodiments are shown in the accompanying figures, it being understood that

the invention is not intended to be limited to the precise arrangements and instrumentalities shown.

[0023] Fig. 1 is a photograph of a cotton textile impregnated with carbon nanotubes, which is shown to be resisting ignition while being exposed to the flame of a propane torch for a duration of less than 10 seconds (Fig. 1A) and between 45 seconds to one minute (Fig. 1B).

[0024] Fig. 2 is a photograph of a cotton textile impregnated with carbon black, which has ignited after exposure to the flame of a propane torch for less than 10 seconds (Fig. 2B) and just before ignition (Fig. 2A).

[0025] Fig. 3 is a photograph of a cotton textile, which has ignited immediately after exposure to the flame of a propane torch (Fig. 3A) and with the flame fully developed and consuming the cotton textile at 45 seconds (Fig. 3B).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0026] The present invention will now be described in detail for specific embodiments of the invention. These embodiments are intended only as illustrative examples and the invention is not to be limited thereto.

One embodiment of the present invention is shown in Fig. 1, which shows a cotton textile that has been impregnated by carbon nanotubes. Carbon nanotubes were mixed with water forming a slurry. Then, the textile was immersed in the slurry, and dried in air. The amount of water used was not critical to the impregnation of the textile, and any quantity of water that makes a slurry could have been used. Indeed, it is possible to impregnate the textile without using any solvent; however, it would be expected that the effectiveness of the flame retardancy could be diminished if the carbon nanotubes were not distributed throughout the textile. Alternatively, the slurry or dry carbon nanotubes could be sprayed onto the textile. However, without limiting the invention in any way, it is believed that the presence of a solvent, such as water, and the type of solvent used can improve the uniformity of carbon nanotube distribution, providing enhanced flame retardancy.

[0027] In a preferred embodiment, the carbon nanotubes are incorporated within the polymer as reinforcing fibers. For example, in oriented polyolefins, which typically have a tensile strength of about 250 N/mm^2, the addition of carbon nanotubes improves the tensile strength by nearly a factor of two, e.g. 400 N/mm^2. The inventors believe that this improvement in strength is caused by the network of fibers within the composite and the oriented crystallization of the polyolefin resin by nucleation on the carbon nanotubes, which provide a template for crystal growth.

[0028] In one embodiment of a flame retardant polymer composite, the carbon nanotubes are selected from single walled nanofibers, multi-walled nanofibers, or fishbone-like graphitic cylinders, exhibiting a hollow core in diameters in the range from 1.2 to 500 nm as an outside diameter. Typically, single walled carbon nanofibers are in the lower end of this range, whereas multi-walled carbon nanofibers and fishbone-like graphitic cylinders throughout the entire range, depending on the processing conditions during fabrication of the carbon nanofibers and subsequent processing conditions.

[0029] Typically, exposure of ultraviolet (UV) light degrades polymers, particularly if bromide flame retardant additives are used. Exposure of a carbon nanotube protected polymeric materials to the UV light of a Xenon light for one month showed no degradation of the physical or mechanical properties of the polymer-carbon nanotube composite. Without limiting the invention, the inventors believe that the carbon nanotubes absorb the UV light preferentially, protecting the polymeric matrix.

[0030] In another embodiment, a multilayered compound structure is fabricated using extrusion and lamination techniques common in the art, wherein a resin sheet layer is sandwiched between thin layers of resin mixed with carbon nanotubes. In a specific embodiment of this invention, a thin decorative surface layer is added on a surface layer of resin mixed with carbon nanotubes. When exposed to a flame, the thin decorative layer vaporizes, but the layer containing carbon nanotubes protects the underlying resin sheet layer from damage by the

flame for up to several minutes. In an alternative embodiment, multiple, alternating layers can be used to impart greater flame retardancy and more isotropic mechanical properties. In one particular embodiment, the polymer matrix is polyoxymethylene (POM) and carbon nanotubes are added in a range between about 0.1% and 60% by volume, preferably from 1 to 40% by volume. More preferably, 25% by volume of carbon nanotubes are added to POM with directionally oriented fibers in the top surface that have an orientation 90 degrees from the direction of the oriented fibers in the bottom surface, and the POM sheet layer is twice as thick as the POM and fiber layers that it is sandwiched between. This particular embodiment provides adequate strength, toughness, and fire retardancy without any additional fire retardant additives, and is useful in parts requiring a wide operating temperature range, e.g. from -100 to +400°C. The selection of a volume percentage of carbon nanotubes in the external layers can be used to regulate the coefficient of thermal expansion of the parts, if compatibility with other parts is desired. Furthermore, the processing into sheets provides both a carbon nanotube orientation and the shear forces necessary to cause de-agglomeration of the carbon nanotubes.

[0031] In yet another embodiment, the dispersion of nanotubes is caused by a separate de-agglomeration step. In one specific embodiment, the carbon nanotubes are treated with an acid, e.g. nitric acid, to create functional groups on the carbon nanotube surface, e.g. carboxylic/acidic functional groups. Then, the carbon nanotubes are rinsed in a solvent, e.g. water, alcohol. The rinsing step may be repeated, including alternating solvents, until the nitric acid is rinsed from the carbon nanotubes. The treated carbon nanotubes can then be dispersed in a solvent using a dispersant, e.g, polyimine derivatives, wherein stirring yields a homogenous slurry and re-agglomeration is prevented. In yet another specific embodiment, stirring is enhanced using ultrasound.

[0032] It should be understood that each embodiment of a method for incorporation of carbon nanotubes within a polymer matrix comprises a specific resin, additives, specific mixing machines, rates of mixing, enhancement by

ultrasound, temperatures, curing times, addition of solvents and other variables, which are specific to particular polymer resins. The specific polymers and resins available are known in the art and curing times and temperatures are readily available or determinable. The inventors have included herein some of the preferred methods for de-agglomeration: using solvents, acids to form functional groups that provide dispersal, spraying, extrusion, mixing and enhanced mixing.

WHAT IS CLAIMED IS:

1. A flame retardant polymer composite comprising:

a polymer composite; and

a plurality of carbon nanofibers, wherein the polymer composite forms a matrix material and the carbon nanofibers reinforce the matrix material, rendering the composite flame retardant.

2. The flame retardant polymer composite of claim 1, wherein the carbon nanofibers are of single walled, multi-walled or fishbone-like graphitic tubes having a hollow core and outer tube diameters in a range of 1.2 to 500 nm.

3. The flame retardant polymer composite of claims 1 and 2, wherein the composite is formed into filaments.

4. The flame retardant polymer composite of claim 3, wherein the filaments are woven into a textile.

5. The flame retardant polymer composite of claims 1 and 2, wherein the composite is formed into a layer.

6. A textile comprising carbon nanofiber reinforced polymeric filaments, wherein the textile is rendered flame retardant.

7. A textile comprising carbon nanofiber impregnated filaments, wherein the textile is rendered flame retardant.

8. The textile of claims 6 and 7, wherein the polymer is an aramid, and the textile resists ballistic impacts.

9. A composite filament comprising at least one carbon nanofiber coated with a polymer, wherein the composite filament is flame retardant.

10. A method for fabricating a flame retardant composite from carbon nanofibers comprising:

treating the carbon nanofibers with an acid, creating functional groups;

rinsing the carbon nanofibers in a solvent;

dispersing the carbon nanofibers in a slurry; and

forming at least one flame retardant layer comprising dispersed carbon nanofibers.

Fig. 1A

Fig. 1B

Fig. 2A

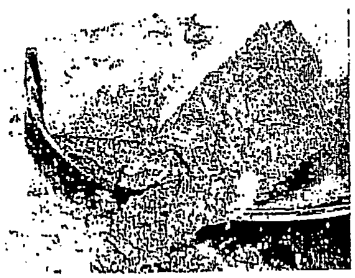

Fig. 2B

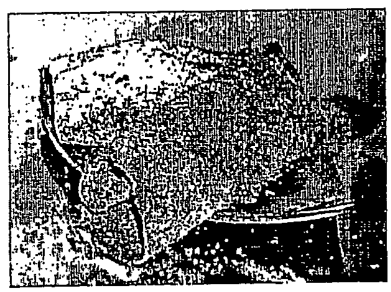

Fig. 3A

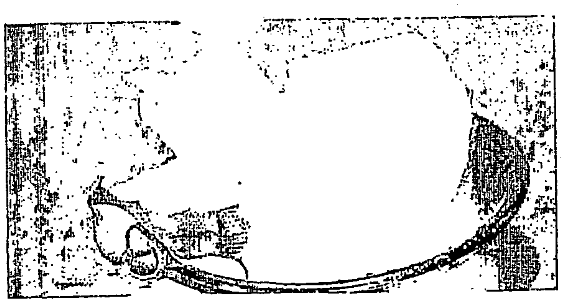

Fig. 3B

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(54) Title: FLAME RETARDANT POLYMER COMPOSITES AND METHOD OF FABRICATION

(57) Abstract: A flame retardant composite and a method for its fabrication are disclosed. The flame retardant composite shows both improved mechanical properties and flame retardancy. The composite comprises a matrix material and carbon nanotubes, such as single walled nanotubes, multi-walled nanotubes or fishbone-like graphitic cylinders, exhibiting a hollow core. For example, the outer diameters of the carbon nanofibers may be in the range from 1.2 to 500 nm. For example, a carbon nanotube may be incorporated as a layer in or on the surface of the composite. The method of fabrication of the composite may include a step of de-agglomeration.

INTERNATIONAL SEARCH REPORT

International Application No
PC.. :B 03/01967

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K7/06 C08K7/24 D01F1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 92381 A (BARRERA ENRIQUE V ;UNIV RICE WILLIAM M (US); LOZANO KAREN (US); CH) 6 December 2001 (2001-12-06) page 5, line 11 - line 32 claims 1-48	1-10
X	WO 01 12700 A (HARWELL JEFFREY H ;UNIV OKLAHOMA STATE (US); NEWMAN GERARD K (US);) 22 February 2001 (2001-02-22) claims 1-10	1-9

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 October 2003	29/10/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Siemens, T

INTERNATIONAL SEARCH REPORT

International Application No
PC.. IB 03/01967

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 199442 Derwent Publications Ltd., London, GB; Class A12, AN 1994-338414 XP002258011 & JP 06 263928 A (BRIDGESTONE CORP), 20 September 1994 (1994-09-20) abstract	1-10

INTERNATIONAL SEARCH REPORT

formation on patent family members

International Application No
PC. 3 03/01967

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0192381	A	06-12-2001	AU	2577101 A	11-12-2001
			CA	2394955 A1	06-12-2001
			CN	1433443 T	30-07-2003
			EP	1244730 A1	02-10-2002
			WO	0192381 A1	06-12-2001
WO 0112700	A	22-02-2001	US	6299812 B1	09-10-2001
			AU	6901600 A	13-03-2001
			WO	0112700 A1	22-02-2001
			US	2001052656 A1	20-12-2001
JP 6263928	A	20-09-1994	NONE		

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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60/358,876 22 February 2002 (22.02.2002) US

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(81) Designated State (*national*): JP.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/072679 A1

(54) Title: MOLECULAR-LEVEL THERMAL-MANAGEMENT MATERIALS COMPRISING SINGLE-WALL CARBON NANOTUBES

(57) Abstract: The present invention relates to devices, processes and materials comprising single-wall carbon nanotubes wherein the single-wall carbon nanotubes serve to transport heat to or from a nanometer scale region wherein that heat is generated or dissipated. Because of their small physical size, excellent heat conductivity, and relatively large surface area, single-wall carbon nanotubes are novel in their function as nanometer-scale agents for heat transport. Appropriately configured in association with a source of heat such as the catalyst for an exothermic polymerization reaction, single wall carbon nanotubes can effectively conduct heat away from the reaction site. This thermal management on a molecular level enables a new class of materials and processes in all areas where heat transport is important. Additionally, new materials such as improved polymer compositions are produced by processes that are thermally-managed at the molecular level by the objects of this invention.

MOLECULAR-LEVEL THERMAL-MANAGEMENT MATERIALS COMPRISING SINGLE-WALL CARBON NANOTUBES

This application claims priority from U.S. provisional application 60/358,876, filed on February 22, 2002, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

This invention relates to devices, materials, and processes comprising single-wall carbon nanotubes wherein the single-wall carbon nanotubes serve to transport heat to or from a nanometer scale region wherein that heat is generated or dissipated. Single-wall carbon nanotubes (SWNT), commonly known as "buckytubes," have been the subject of intense research since their discovery due to their unique properties, including high strength, stiffness, and thermal and electrical conductivity. SWNT are fullerenes consisting essentially of sp^2-hybridized carbon atoms typically arranged in hexagons and pentagons. For background information on single-wall carbon nanotubes, see B.I. Yakobson and R. E. Smalley, *American Scientist*, Vol. 85, July-August, 1997, pp. 324-337. Multi-wall carbon nanotubes are nested single-wall carbon cylinders and possess some properties similar to single-wall carbon nanotubes. However, since single-wall carbon nanotubes have fewer defects than multi-wall carbon nanotubes, the single-wall carbon nanotubes are generally stronger and more conductive, both thermally and electrically. Additionally, single-wall carbon nanotubes have considerably higher available surface area per gram of carbon than multi-wall carbon nanotubes.

In many electrical, chemical and physical processes, heat is generated or required in nanometer-scale regions, often by molecular-level interactions of a chemical or physical nature. In circumstances where heat is generated, that heat often has detrimental effects and must be removed from the process. In processes where heat is required, it is most preferable that the heat be delivered at a precise location on a molecular scale, but that, heretofore, has generally been impossible. Even though heat is generated or required by specific molecular-level interactions, the transport of heat in most chemical and physical processes is provided through its transport in bulk materials. Therefore, it is anticipated that the art of chemical and physical processes will be advanced by an invention that enables enhanced transport of heat generated or required in molecular-level interactions, particularly if those means operate at the nanometer scale.

SUMMARY OF THE INVENTION

This invention relates to devices, materials, and processes that incorporate single-wall carbon nanotubes as heat transfer agents to improve the efficacy of heat transport to and from nanometer-scale regions. A nanometer-scale region, for the purposes of this invention, is one contained within a sphere of 30 nanometers in diameter, more preferably 10 nanometers in diameter, and most preferably 3 nanometers in diameter. Said nanometer-scale region can contain either a heat source or a heat sink. Molecular-level processes that act as heat sources or heat sinks occur within such nanometer-scale regions. If a portion of one or more single-wall carbon nanotubes lies within this nanometer-scale region, it can dispense or absorb heat there and effectively transport heat to or from that region. This invention enables a new level of heat transfer engineering in many bulk-scale chemical and physical processes, by providing for thermal management at the molecular level.

One embodiment of the invention is a molecular level thermal management device comprising at least one single wall carbon nanotube. In this device, at least some portion of a single-wall carbon nanotube shares a nanometer-scale region with a heat source, the single-wall carbon nanotube is in contact with an environment to which it can transfer heat, and the single-wall carbon nanotube transfers heat from the heat source to said environment.

Another embodiment of the invention is a molecular level thermal management device comprising at least one single wall carbon nanotube. In this device, at least some portion of a single-wall carbon nanotube shares a nanometer-scale region with a heat sink, the single-wall carbon nanotube is in contact with an environment from which it can receive heat, and the single-wall carbon nanotube transfers heat from said environment to the heat sink.

Another embodiment of the invention is a polymerization catalyst system that comprises a polymerization catalyst and a plurality of single-wall carbon nanotubes. Additional embodiments are a polymerization process, wherein at least one monomer is polymerized in the presence of the catalyst system, and the polymer produced by that process.

Another embodiment of the invention is a fixed-bed polymerization reactor. The reactor comprises at least one fixed-bed that comprises at least one polymerization catalyst attached to single-wall carbon nanotubes. The nanotubes are formed into a macroscopic porous structure, which allows diffusion of at least one monomer to an active polymerization site on the polymerization catalyst and transport of at least one polymer and heat away from the active site and out of the fixed-bed.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

Various embodiments of this invention use single-wall carbon nanotubes to enable transport of heat to or from a nanometer scale region. Implementation of this nanometer-scale heat transport enables new devices, materials, and processes.

For clarity in the following description, however, this invention will initially be discussed with respect to an embodiment where single-wall carbon nanotubes serve to remove heat from a nanometer-scale region where the heat is being produced. In this embodiment, some portions of single-wall carbon nanotubes are placed in close proximity to the region of heat generation, and other portions of said nanotubes lie between that region and an environment that enables removal of heat from the single-wall carbon nanotube surface. In this embodiment, single-wall carbon nanotubes are molecular-level heat transfer conduits that enable heat removal from heat-generating molecular-level processes. Single-wall carbon nanotubes are individual molecules that are excellent conductors of heat. The small physical size of single-wall carbon nanotubes permits portions of them to be located in contact with or in very close proximity to the heat source. Heat from the source can be transferred to the single-wall carbon nanotubes through any of the known means of thermal energy transfer, including, but not limited to, convection, radiation, vibrational energy transfer, electronic energy transfer, mass transfer and accommodation, molecular heat conduction, and combinations thereof. Upon receiving the heat energy within the nanometer-scale region, the single-wall carbon nanotubes will then efficiently conduct heat away from the nanometer-scale region and distribute that heat over the single-wall carbon nanotube surface. If that surface is in an environment where heat can be removed from that surface, then the locally-generated heat will be effectively dissipated, and the temperature at the heat-generation region will be lowered. The environment for heat removal is one that allows transfer of heat from the single-wall carbon nanotube surface by any of the known means of thermal energy transfer, including, but not limited to, convection, radiation, vibrational energy transfer, electronic energy transfer, mass transfer and accommodation, molecular heat conduction, and combinations thereof. The device of this invention can comprise more than one single wall carbon nanotube and heat can be transferred from one single-wall carbon nanotube to another as it is transported. Single-wall carbon nanotubes are particularly effective in redistribution of heat because they are nanometer scale structures with excellent thermal conductivity and relatively large surface areas.

One embodiment of the heat-removal device described above is a catalyst system for an exothermic polymerization process. In this embodiment, the catalyst system comprises

single-wall carbon nanotubes and a polymerization catalyst wherein the single-wall carbon nanotubes are directly associated with the catalyst. This association can, without limitation, include physisorption, chemisorption, and/or chemical bonding of the single-wall carbon nanotubes to the catalyst. The chemical bonding can be covalent, ionic or a combination of both, and can occur on the single-wall carbon nanotubes' open ends, closed ends, side walls, defects in the side walls and combinations thereof. This catalyst system composition enables formation of new high-molecular weight polymers, improved polymerization processing methods, and new composite compositions comprising single-wall carbon nanotubes and polymers. During the polymerization process the catalyst participates in an exothermic polymerization reaction forming a polymer material, and the local heat produced in a nanometer-scale region containing the catalyst is carried away by the nanotube material.

Another embodiment of this invention is a material comprising the devices described above. For instance, one can create a bulk composition comprised of single-wall carbon nanotube material combined with entities which serve as a heat sources or sinks. Such a composition could, for instance, be a material comprising single-wall carbon nanotubes with a catalyst that can participate an exothermic chemical reaction.

Another embodiment of this invention is a process utilizing one or more of the devices of this invention, and products of that process. One example would be the polymerization process for polyolefins discussed in Example 1, and products of that process.

This invention admits many variations. In other embodiments, the highly porous nature of single-wall carbon nanotube mats and felts can enable new types of polymerization reactors, such as fixed bed reactors, micro-reactors, catalyst support films, and chemically-active materials comprising the present invention. Suspended single-wall carbon nanotube catalysts with polymers adsorbed on or wrapped around the nanotubes can be left in the polymer material to provide new compositions of polymers reinforced with highly dispersed nanotubes. Because of the intimate proximity of the single-wall carbon nanotube structure to the polymerization site, these materials have enhanced polymer alignment and comprise polymers with molecular weights and mechanical properties enhanced over those produced by other polymerization procedures. Such new compositions will have improved properties such as strength, electrical conductivity and processability into stronger films and fibers. More generally, this invention admits the fabrication of a wide range of materials and devices where thermal management is important on a nanometer scale.

Other examples include providing heat to endothermic reactions wherein the catalytic entity is placed near the end of a single-wall carbon nanotube or bundle of such nanotubes.

Yet other examples include placing one or more single-wall carbon nanotubes with one or more of their ends in proximity to one or more electronic devices (e.g. transistors, diodes, multi-junction devices, resistors, thermistors, sensors, reactive elements, transducers, memory elements, and combinations thereof) in semiconductor electronics assemblies wherein the single-wall carbon nanotubes are added during an appropriate processing step. In this embodiment, the single wall carbon nanotubes carry away heat generated in junctions in the semiconductor assemblies. Another example is in the creation of high-energy materials, such as explosives, rocket fuel and incendiary chemicals where one seeks to control the burning rate by molecular-level thermal management. In other applications for energy-absorbing materials, molecular-level thermal management can provide heat conduction that enables a chemical reaction front to propagate through a material, enabling dissipation of energy in the material. This application of the invention is particularly useful in auto bodies and armor, and other materials designed to absorb energy in a controlled-failure scenario.

In one embodiment, single-wall carbon nanotubes are incorporated in an olefin polymerization catalyst system to provide a more effective catalytic process. Another embodiment of the invention comprises improved polymer compositions generated by such a catalyst system. In one particular embodiment, for example, a device comprises single-wall carbon nanotubes that are configured in proximity to nanometer-scale regions where heat is generated during a process. Here, that configuration can be fabricated by contacting an olefin polymerization catalyst with single-wall carbon nanotubes ends, sides or combinations thereof. Another embodiment of the invention is a material comprising such devices. A further embodiment of the invention is a method that uses said material in a chemical process, such as the production of a polyolefin. Another embodiment of the invention comprises any product of that production process. These products can include polyolefin materials whose properties exceed those of known polyolefin materials in the areas of molecular weight, molecular orientation, strength, toughness, and thermal stability. This method of polyolefin production also naturally produces a material which is a composite of polyolefin polymer and single-wall carbon nanotubes, and that material and the process for its production are also embodiments of this invention.

Olefin polymerization catalysts are known to those skilled in the art of manufacturing polyethylene, polypropylene, polybutenes, polyisobutylenes, polystyrenes and various copolymers, such as ethylene-butene copolymers, ethylene-propylene copolymers and terpolymers, isobutylene-isoprene copolymers (butyl rubber) and other polymers. Such

polymerization catalysts include aluminum, magnesium and titanium halides, conventional Ziegler-Natta, newer metallocene and other "single-site" catalysts such as zirconium- and titanium-based metallocenes with alumoxane or other non-coordinating anionic co-catalysts, such as perfluorophenyl borane compounds.

Association of chemical entities with single-wall carbon nanotubes can be done by means known to those skilled in the art. Examples of association include chemical bonding, van der Waals interactive forces, polar interactions, and indirect contact through other materials.

Incorporation of single-wall carbon nanotubes in olefin polymerization catalyst systems provides an improved catalyst composition that has functionality previously unknown in olefin polymerization catalysts. This functionality derives from the ability of the single-wall carbon nanotubes to receive and transfer heat away from the point at which the polymerization reaction is occurring. Additionally this invention includes a composition of matter comprising association of a catalytic moiety (such as an olefin polymerization catalyst) with one or more single-wall carbon nanotubes that serve as a "molecular-level heat transfer agent".

Olefin polymerization is a highly exothermic reaction. The heat generated when the monomer reacts with the catalyst and is inserted into the growing polymer chain must be transferred away from the catalyst site. If this is not done, a runaway reaction can result as the catalyst heats up and the reaction proceeds faster releasing more heat. To control heat generation, catalysts and reactor systems are designed to limit the rate of polymerization. In addition, local heating at the catalyst site can cause limitations in the molecular weight of the polymers made because, at elevated temperatures, the rates of termination reactions increase in comparison to the rates for propagation (chain growth) reactions. Furthermore, local heating can cause catalyst deactivation. By conducting heat away from the catalyst site, the single-wall carbon nanotubes will allow higher molecular weight polymers to be made at faster rates and with less catalyst deactivation. Additionally, the enhanced molecular-level thermal management provided by the catalyst composition described here helps ensure a more uniform temperature throughout the polymerization section of the reactor and mitigates against formation of "runaway hot spots" in the reactor where polymer growth termination and unwanted catalyst deactivation can occur.

The preceding description of specific embodiments of the present invention is not intended to be a complete list of every possible embodiment of the invention. Persons skilled

in this field will recognize that modifications can be made to the specific embodiments described here that would be within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A molecular level thermal management device comprising at least one single wall carbon nanotube, wherein:

   at least some portion of a single-wall carbon nanotube shares a nanometer-scale region with a heat source,

   the single-wall carbon nanotube is in contact with an environment to which it can transfer heat, and

   the single-wall carbon nanotube transfers heat from the heat source to said environment.

2. The device of claim 1, wherein the single-wall carbon nanotube is in contact with the heat source.

3. The device of claim 1, wherein the heat source is a chemical reaction.

4. The device of claim 1, wherein the heat source is an electronic device.

5. The device of claim 1, wherein the device forms part of a fixed-bed reactor, a micro-reactor, a catalyst support structure, or a semiconductor electronic assembly.

6. A material comprising at least one device of claim 1.

7. A molecular level thermal management device comprising at least one single wall carbon nanotube, wherein:

   at least some portion of a single-wall carbon nanotube shares a nanometer-scale region with a heat sink,

   the single-wall carbon nanotube is in contact with an environment from which it can receive heat, and

   the single-wall carbon nanotube transfers heat from said environment to the heat sink.

8. The device of claim 7, wherein the single-wall carbon nanotube is in contact with the heat sink.

9. The device of claim 7, wherein the heat sink is a chemical reaction.

10. The device of claim 7, wherein the heat sink is an electronic device.

11. The device of claim 7, wherein the device forms part of a fixed-bed reactor, a micro-reactor, a catalyst support structure, or a semiconductor electronic assembly.

12. A material comprising at least one device of claim 2.

13. A polymerization catalyst system comprising a polymerization catalyst and a plurality of single-wall carbon nanotubes.

14. The polymerization catalyst system of claim 13, wherein the polymerization catalyst is adapted to catalyze olefin polymerization.

15. A polymerization process, wherein at least one monomer is polymerized in the presence of a catalyst system that comprises a polymerization catalyst and a plurality of single-wall carbon nanotubes.

16. The process of claim 15, wherein the polymerization process forms at least one polyolefin.

17. A polymer produced by polymerization of at least one monomer in the presence of a polymerization catalyst system that comprises a polymerization catalyst and a plurality of single-wall carbon nanotubes.

18. The polymer of claim 17, wherein at least one monomer is an olefin and the polymer is a polyolefin.

19. A high-energy material comprising at least one device according to claim 1, and at least one explosive, rocket fuel, incendiary chemical, or combination thereof.

20. A high-energy material comprising at least one device according to claim 7, and at least one explosive, rocket fuel, incendiary chemical, or combination thereof.

21. A fixed-bed polymerization reactor that comprises at least one fixed-bed that comprises at least one polymerization catalyst attached to single-wall carbon nanotubes which are formed into a macroscopic porous structure which allows diffusion of at least one monomer to an active polymerization site on the polymerization catalyst and transport of at least one polymer and heat away from the active site and out of the fixed-bed.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/05254

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K5/14 C08F4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HAFNER J H ET AL: "CATALYTIC GROWTH OF SINGLE-WALL CARBON NANOTUBES FROM METAL PARTICLES" CHEMICAL PHYSICS LETTERS, NORTH-HOLLAND, AMSTERDAM, NL, vol. 296, no. 1/2, 30 October 1998 (1998-10-30), pages 195-202, XP000869784 ISSN: 0009-2614 page 196 -page 198 ---	13
X	WO 95 10481 A (DU PONT) 20 April 1995 (1995-04-20) the whole document ---	13

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 June 2003	13/06/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Puetz, C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/05254

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YAKOBSON B I ET AL: "FULLERENE NANOTUBES: C1,000,000 AND BEYOND SOME UNUSUAL NEW MOLECULES-LONG, HOLLOW FIBERS WITH TANTALIZING ELECTRONIC AND MECHANICAL PROPERTIES-HAVE JOINED DIAMONDS AND GRAPHITE IN THE CARBON FAMILY" AMERICAN SCIENTIST, NEW HAVEN, CT, US, vol. 85, no. 4, July 1997 (1997-07), pages 324-337, XP001025773 ISSN: 0003-0996 cited in the application page 335, left-hand column ---	7,8,10
P,X	DE 100 48 406 A (INFINEON TECHNOLOGIES AG) 6 June 2002 (2002-06-06) column 1, line 35 -column 2, line 44 column 3, line 35 -column 4, line 14 column 5, line 49 -column 6, line 22 claims 1,8-12,20,21 ---	13
A	EP 1 059 266 A (ILJIN NANOTECH CO LTD ;LEE CHEOL JIN (KR)) 13 December 2000 (2000-12-13) claims 1,2 -----	13

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-21

Present claims 1-16 and 19-21 relate to an extremely large number of possible devices, materials, polymerization catalyst systems and polymerization processes. In fact, the claims contain so many options that a lack of clarity and conciseness within the meaning of Article 6 PCT arises. Furthermore no embodiment has been disclosed in a manner sufficientely clear and complete for a skilled person to reduce the intended technical teaching to practice, at least not without undue burden of experimentation; the application lacks disclosure within the meaning of Article 5 PCT to such an extent that a meaningful search for the numerous claims across their whole breadth is not possible. Consequently, the search has been carried out for those parts of the application which do appear to be clear and concise, namely polymerization catalyst systems, wherein the polymerization catalyst is in contact with single-wall carbon nanotubes and the use of said catalyst systems to catalyze olefin polymerizations (see page 5, line 15 - page 6, line 31). The other stated applications (see page 5, lines 1-14) have been regarded as being merely speculative and not being disclosed and supported by the present application within the sense of Articles 5 and 6 PCT, and thus not searched.

Furthermore no search at all has been performed for claims 17 and 18. These claims for products are only defined in terms of their process of manufacture, without indicating any clear product feature that would enable a meaningful search; moreover said claims lack support and disclosure within the meaning of Articles 6 and 5 PCT to such an extent that a meaningful search is impossible.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/05254

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.: 1-21
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 03/05254

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9510481	A	20-04-1995	WO	9510481 A1	20-04-1995
DE 10048406	A	06-06-2002	DE	10048406 A1	06-06-2002
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			EP	1059266 A2	13-12-2000
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